

New Techniques in Characterization of Ferroelectric Materials

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Two new techniques have been developed to characterize $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) based ferroelectric single crystals: (i) electro-thermal imaging, and (ii) single crystal x-ray diffraction in the transmission mode.

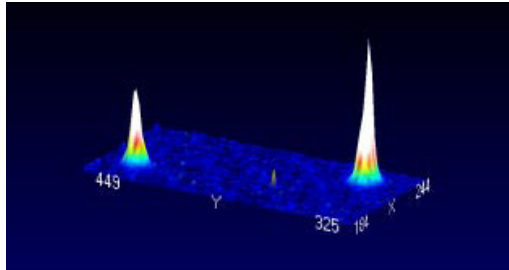
(i) Electro-thermal imaging is a remote sensing technique that can detect the polarization direction and poling state of a whole crystal slice. This imaging technique utilizes an IR camera to determine the field induced temperature change and does not require any special or destructive sample preparation. In the resulting images it is possible to distinguish regions of 180° domains. This powerful technique can be used remotely during poling to determine the poling state of the crystal to avoid over-poling that can result in inferior properties and/or cracking of the crystals. Electro-thermal imaging produced the first direct observations of polarization rotation. Under bipolar field, the domains near the corners were the first to switch direction. As the field increased above the coercive field, domains at the center part of the crystals switched direction.

(ii) X-ray diffraction in the transmission mode has long been used in structure determination of organic crystals and proteins; however, it is not used much to characterize inorganic systems. $0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.3\text{PbTiO}_3$ single crystals were examined by this XRD technique for the first time, and a never-before-seen super-lattice was revealed with a doubling of the unit cell in all three directions, giving a cell volume eight times that of a traditional perovskite unit cell. The significance of the super-lattice peaks increased with poling, indicating a structural contribution to ordering. Lack of such observations by electron diffraction in the transmission electron microscope examinations suggests the presence of a bulk effect.

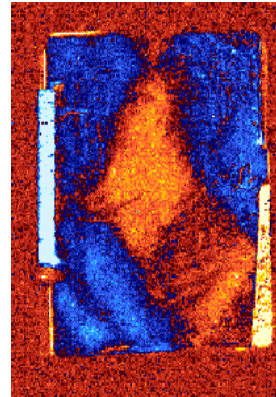
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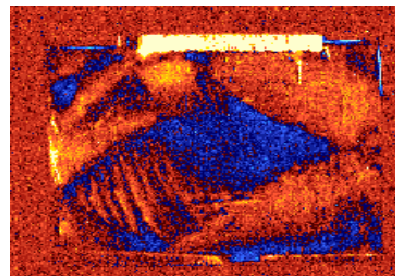
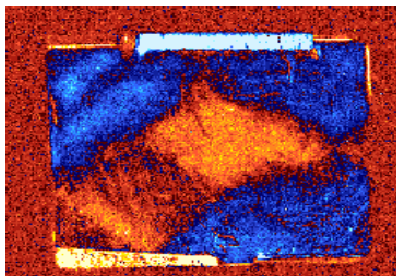
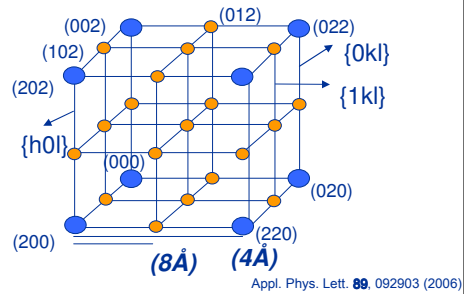
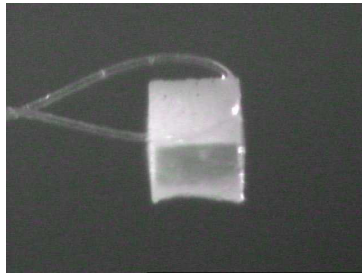
NASA Glenn Research Center and
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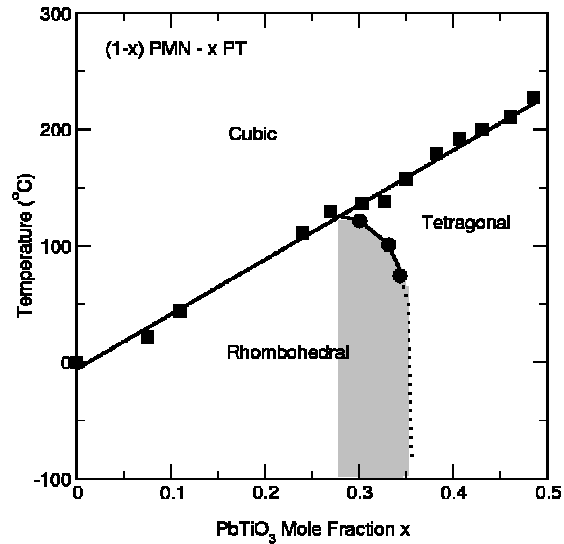
H.C. Materials Corp.



Outline

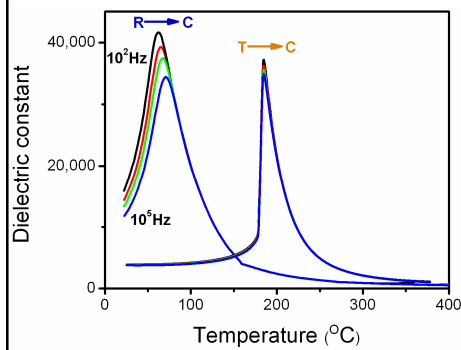


PMN-PT single crystals

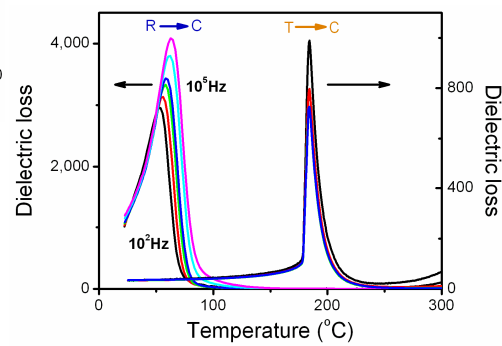
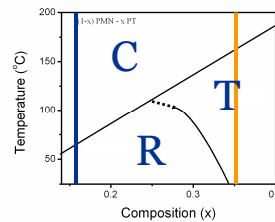


Shrout T., Zeng P. C., Namchul K., Markgraf S. *Ferroelectrics Letters* **12**: 63-69, 1990.

Outside the MPB region, $\langle 001 \rangle$ direction

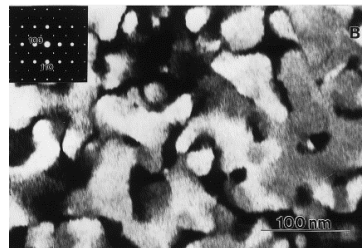
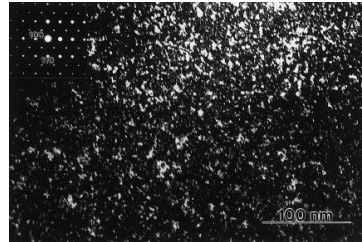


Unpoled



Ordering

- Relaxor $\text{Pb}(\text{Me}^{2+}_{1/3}\text{Me}^{5+}_{2/3})\text{O}_3$
i.e., PMN, PMT
- Superlattice B' , B'' (1:1) sites
- Theories
 - Space-charge model
 $\text{B}' = \text{Me}^{2+}$, $\text{B}'' = \text{Me}^{5+}$
in Me^{5+} rich matrix
 - Random site model
 $\text{B}' = \text{Me}^{5+}$, $2/3\text{B}'' = \text{Me}^{2+}$, $1/3\text{B}'' = \text{Me}^{5+}$
- Ordered relaxors
- $\text{B}_{1/2}$, $\text{B}_{1/2}$ perovskites. i.e., $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$
- Chemical ordering / Structural ordering
- PMN-PT, decreasing superlattice intensity with increasing PT content



W. Dmowski, M. K. Akbas, T. Egami and P. K. Davies *Journal of Physics and Chemistry of Solids* Volume 63, Issue 1, January 2002, Pages 15-22

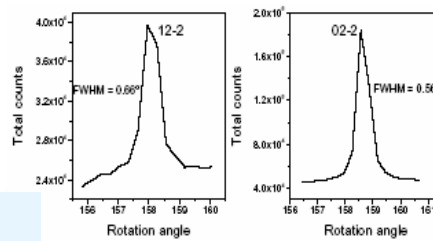
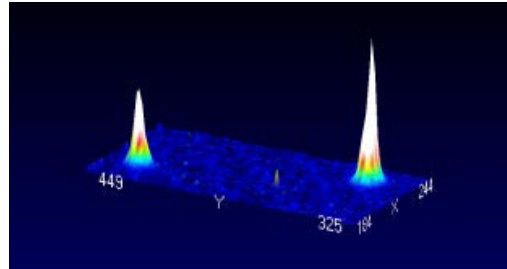
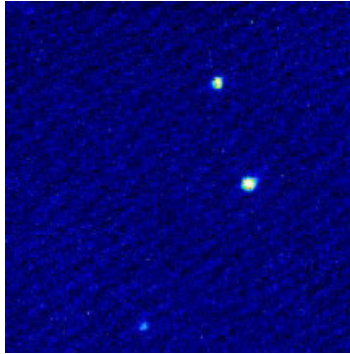
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XRD in the transmission mode

- Advantages
 - enables a large number of diffraction peaks to be collected from a single crystal (without destructive sample preparation)
 - measurements can be conducted on the same crystal both in poled and unpoled states
 - less problem with surface effects
- Disadvantages
 - absorption of X-rays by Pb and Nb.
 - *can be corrected for absorption by the new software technology*
 - *small crystal size for shorter path*
- Software
 - Bruker molecular analysis research tool (SMART)
 - Three dimensional profile analysis (SAINT)
 - Absorption correction (SHELXTL/XPREP)

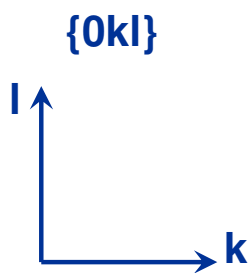
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XRD (in the transmission mode) - peaks



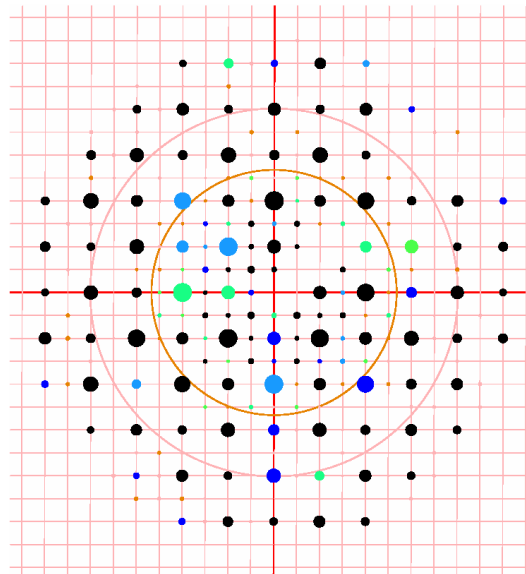
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Reciprocal lattice (poled along $\langle 111 \rangle$)

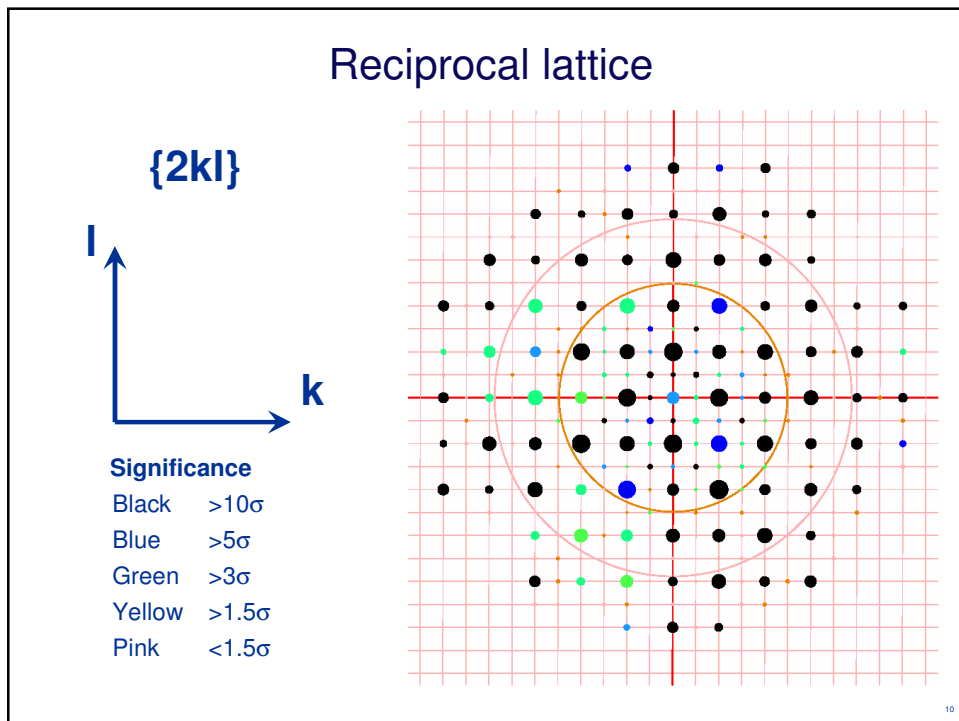
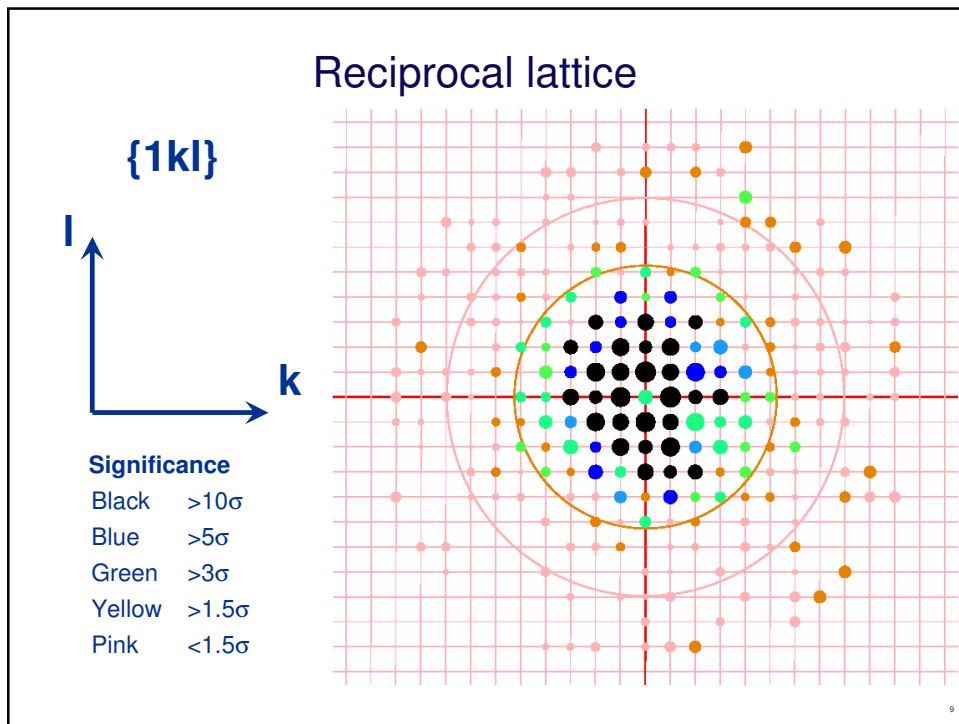


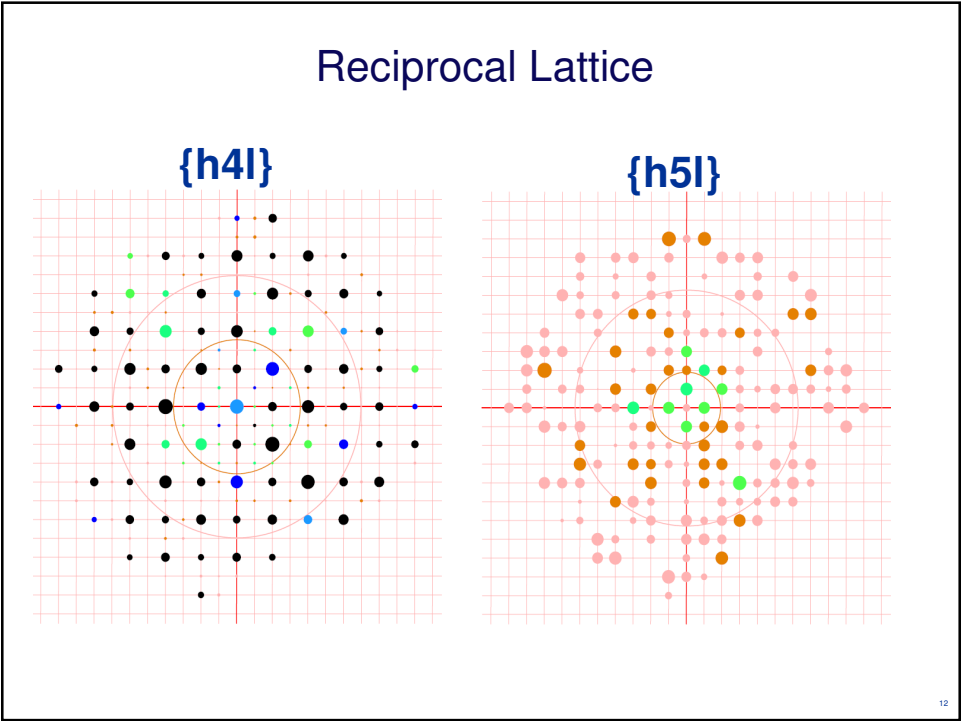
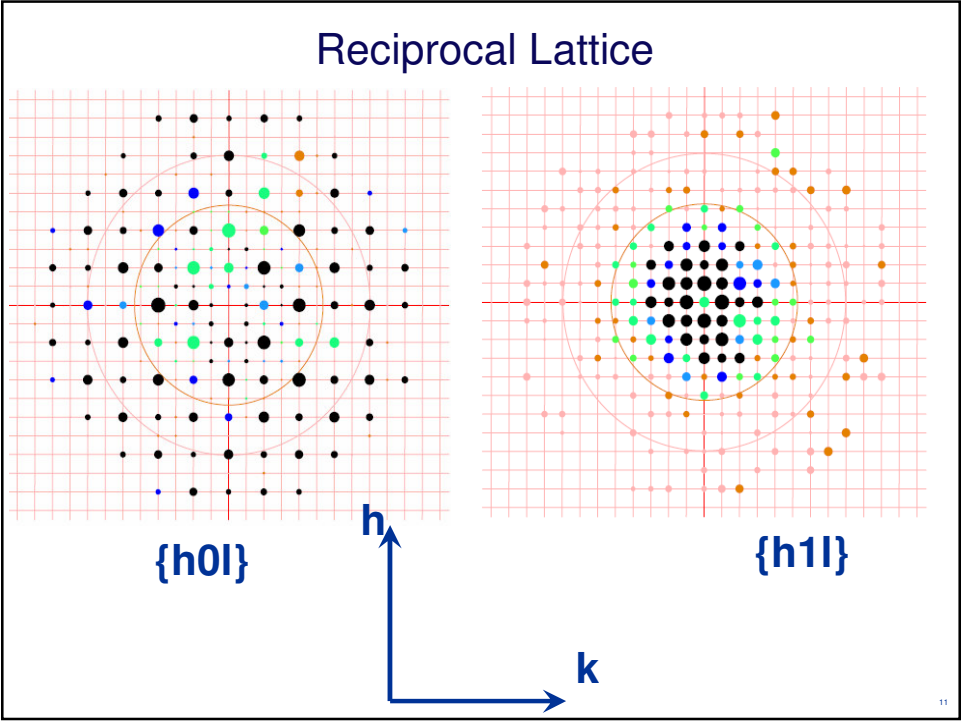
Significance

- Black $>10\sigma$
- Blue $>5\sigma$
- Green $>3\sigma$
- Yellow $>1.5\sigma$
- Pink $<1.5\sigma$

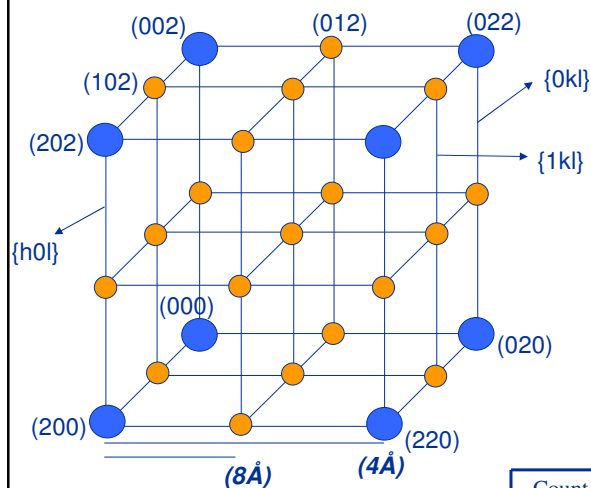


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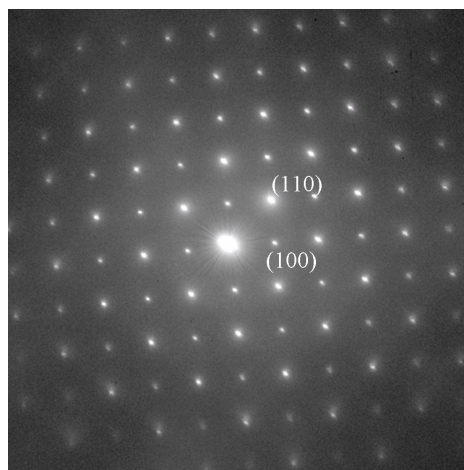
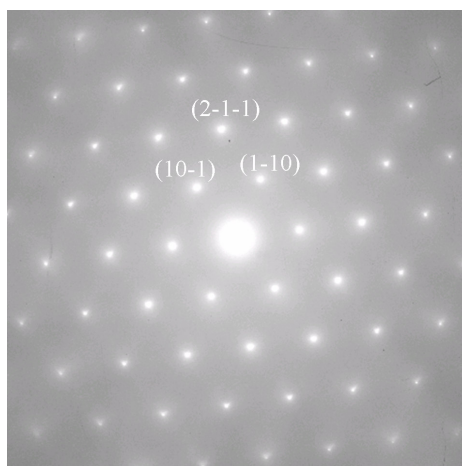
Reciprocal lattice – 3D



| Reflection | I (σ) |
|-----------------------|----------------|
| $\langle 110 \rangle$ | 152 (4) |
| $\langle 013 \rangle$ | 57 (4) |
| $\langle 100 \rangle$ | 52 (2) |
| $\langle 111 \rangle$ | 75 (3) |

| | Poled along $\langle 111 \rangle$ | | Unopled | |
|------------------------------|-----------------------------------|------------|-----------|------------|
| | Odd peaks | Even peaks | Odd peaks | Even peaks |
| Count of peaks | 1053 | 148 | 1053 | 150 |
| $\langle I \rangle / \sigma$ | 6 | 112 | 3 | 113 |

TEM - electron diffraction



Conclusions

- XRD in the transmitting mode was applied to characterize PMN-PT single crystals.
- All the reflection can be obtained from one single crystal.
- Sample preparation in non-destructive making it possible to study the crystal both in poled and unpoled states.
- A never before seen superlattice was detected for the compositions in the MPB region.
- Poling increased the significance of the superlattice.
- Such superlattice peaks were not observed by TEM indicating a possible bulk-effect.

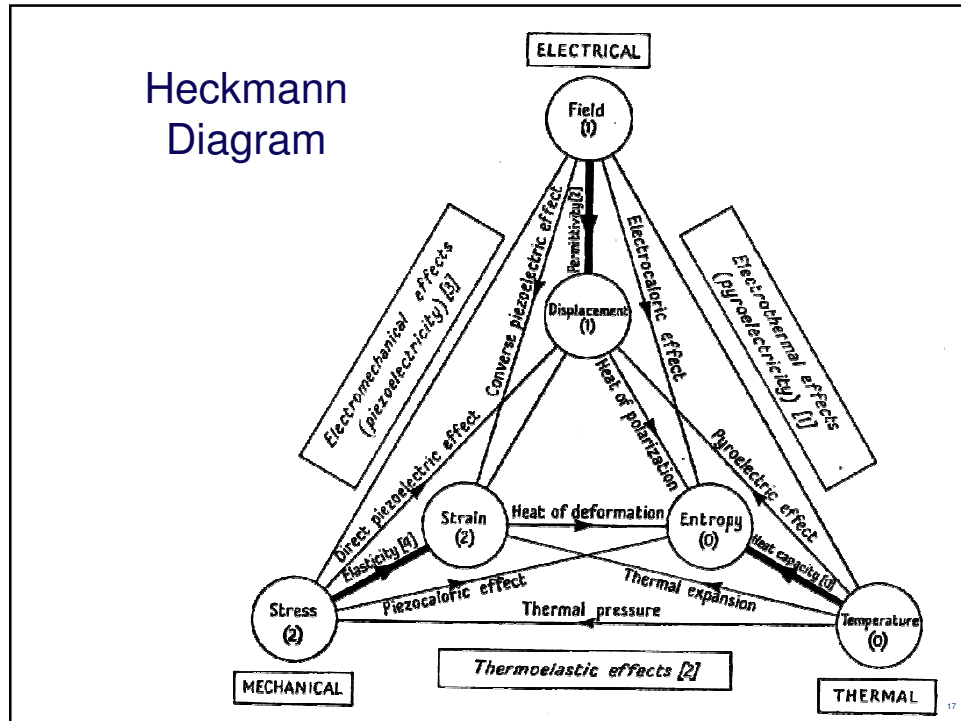
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Electro-thermal Imaging

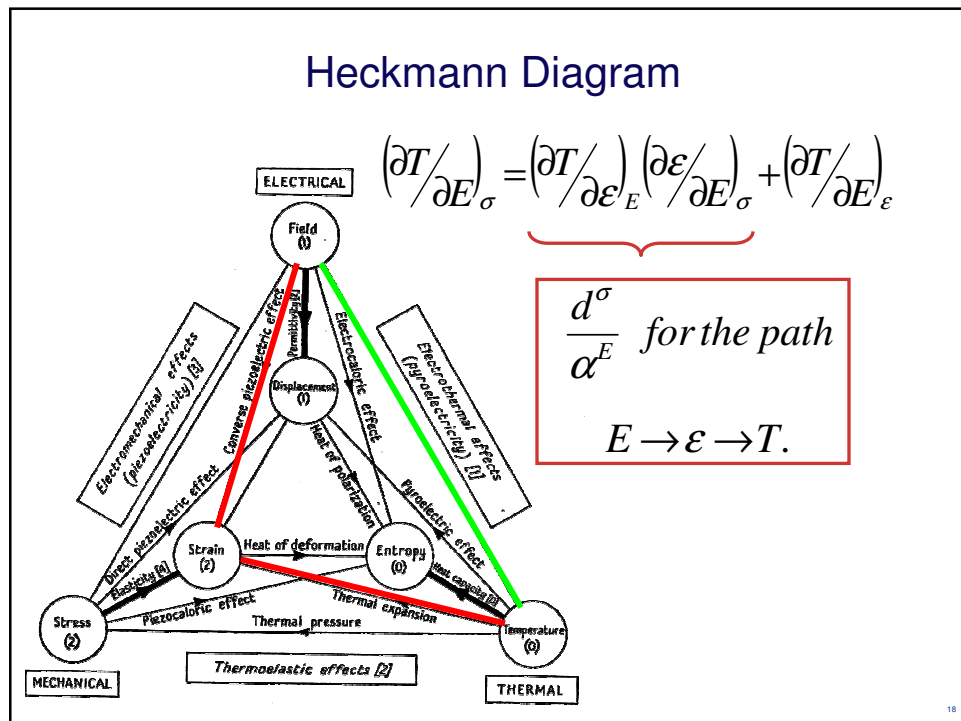
- Field-induced temperature changes
- Material ($0.68 \text{ Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.32 PbTiO_3 (68PMN-32PT) single crystal - $\langle 001 \rangle$ orientation, 1x2x0.15 cm size)
- Experimental
- Results
 - Effect of electrode material
 - Poling state
 - Polarization switching
 - Sign of the poling direction

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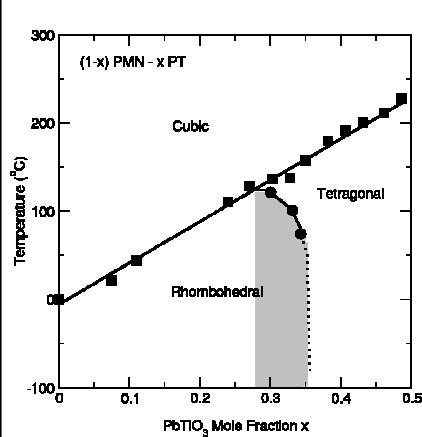
Heckmann Diagram



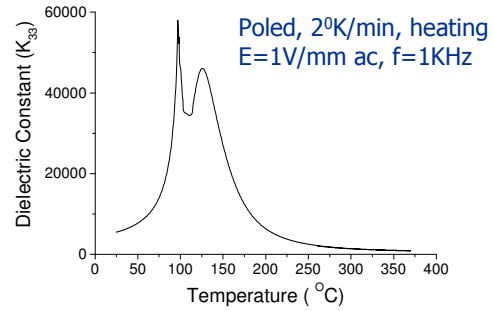
Heckmann Diagram



Material (68PMN-32PT)



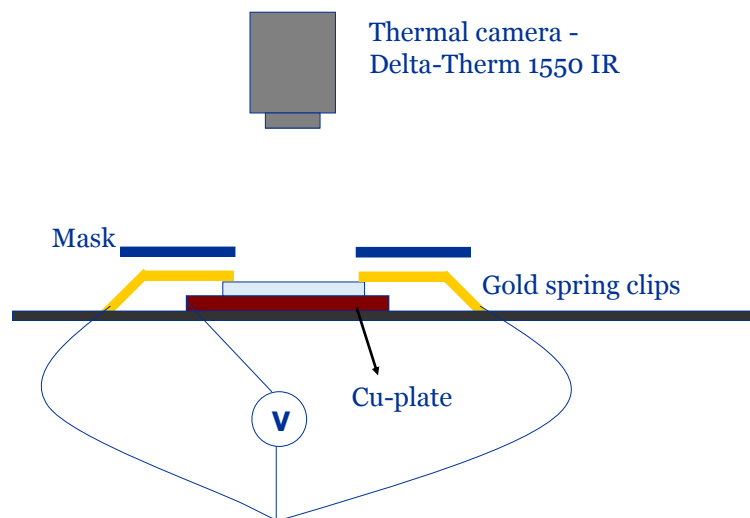
Shrout T., Zung P. C., Namchul K., Markgraf S.
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- Ferroelectric material
- Composition in morphotropic phase boundary(MPB) region
- Remarkable piezoelectric properties in the MPB region.

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Experiment



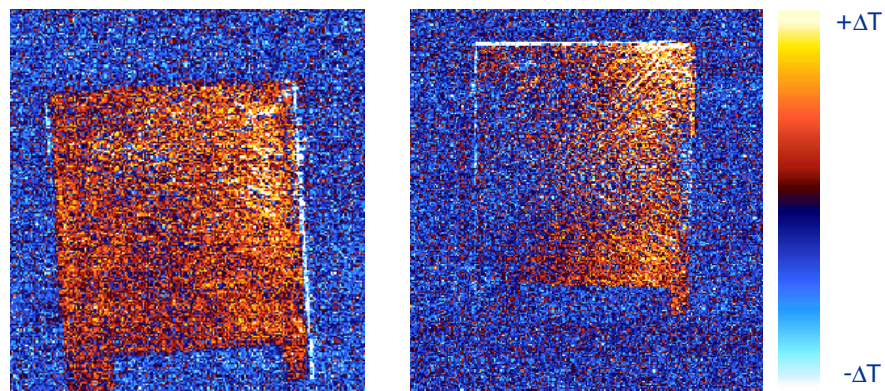
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Electro-thermal imaging

- Material: 68PMN-32PT single crystal
 <001> orientation, 1x2x0.15 cm size
- Spatial resolution=110 microns
- 75 V sinusoidal voltage at 100 Hz to induce T-change
- IR images at the same frequency as the applied voltage
- Temperature resolution of 0.003 K
- 1 minute for data collection

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Effect of electrode material



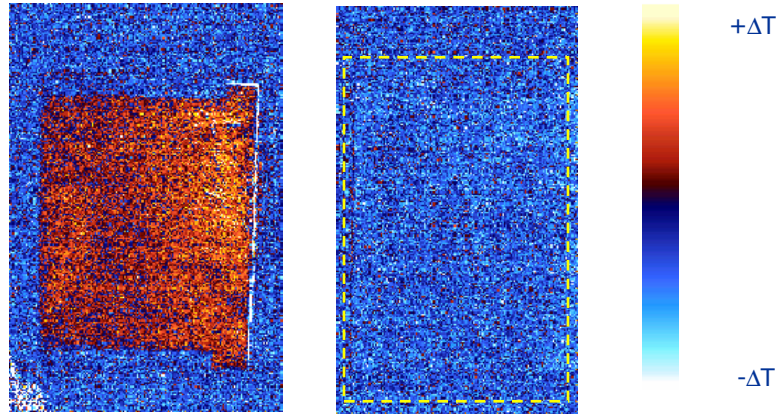
Carbon

Gold

Higher emissivity for Carbon

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Poled vs. Unpoled



- Poled : Oriented domains; same sign of response
- Unpoled: Random domains; overall response is near zero, same as the background where $\Delta T = 0$

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Polarization Reversal

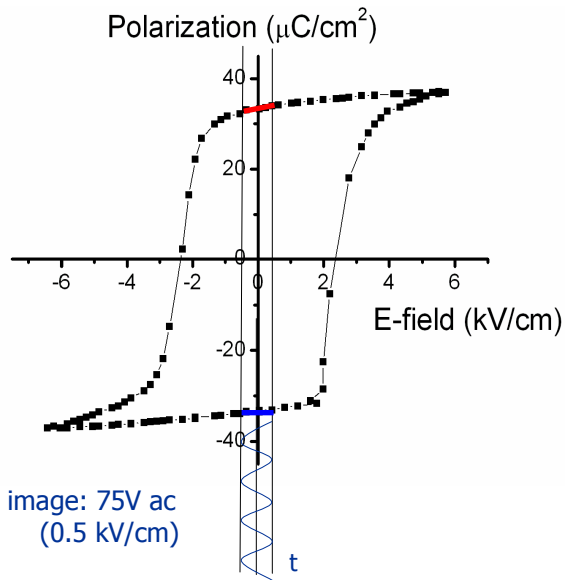
- Sample size 1 x 2 x 0.15 cm
- Initial poling at +750 V dc and 25°C
- Reverse poling by gradually changing negative dc field with current limitation
- Application of 75 V ac 100 Hz to induce the temperature change.

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Polarization vs. E-field

$$E_c = 2.4 \text{ kV/cm}$$

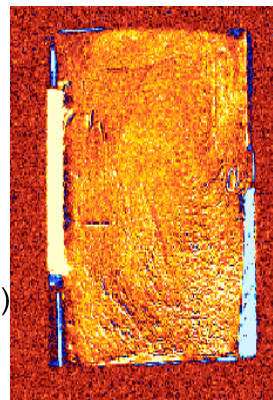
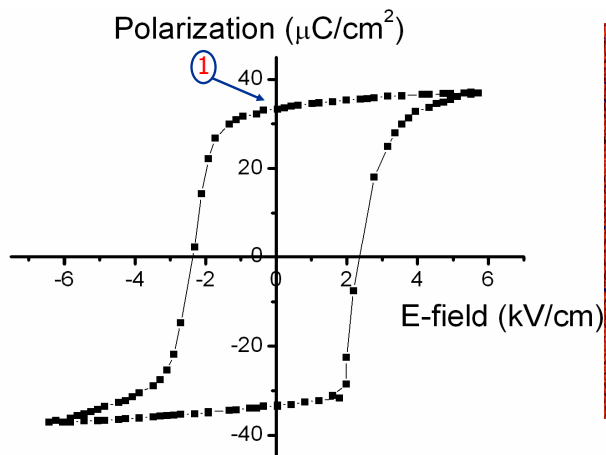
$$P_R = 33.3 \text{ } \mu\text{C/cm}^2$$



Voltage applied to take the image: 75V ac
(0.5 kV/cm)

25

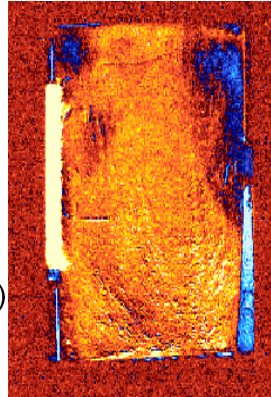
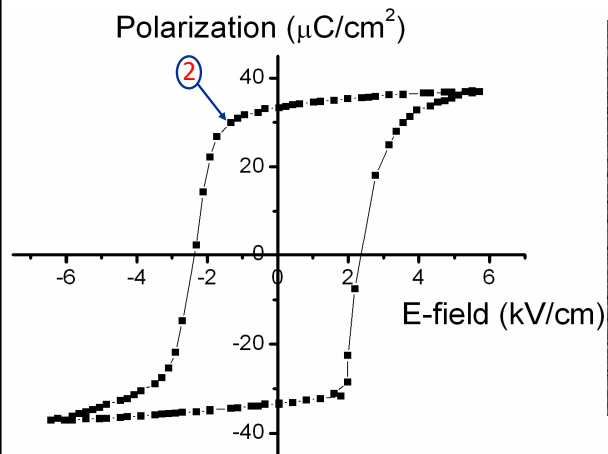
Polarization vs. Field



•Measured by RT66A

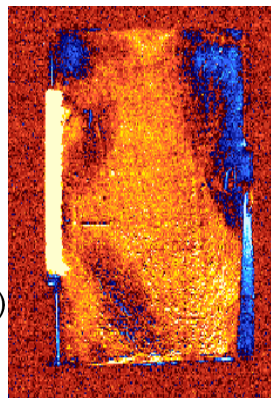
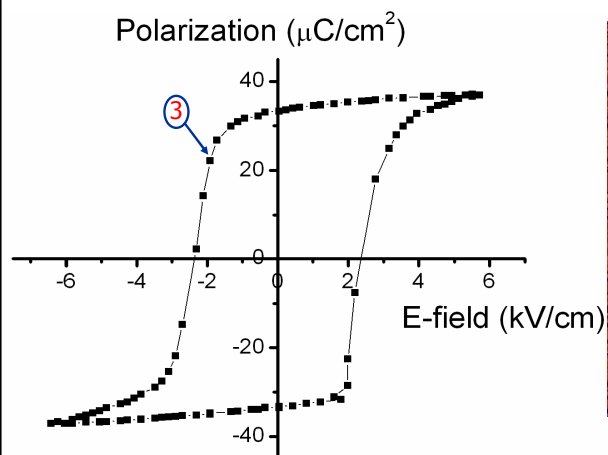
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Polarization vs. Field



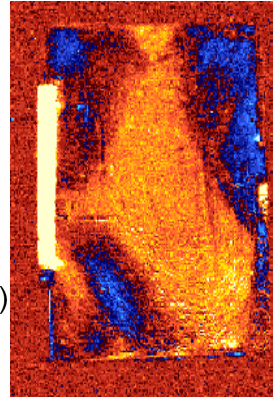
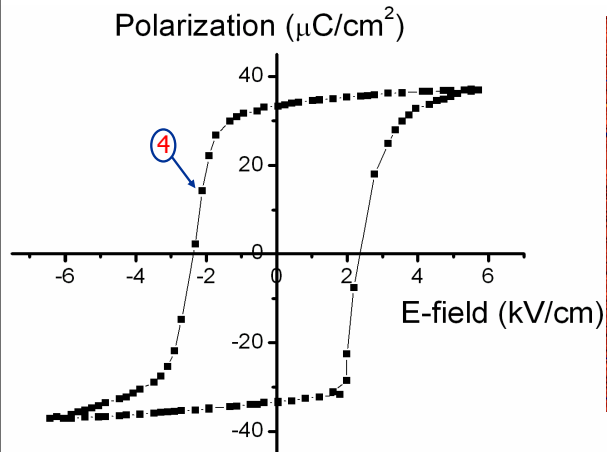
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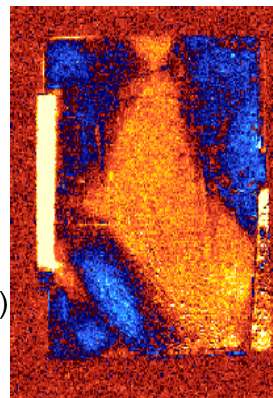
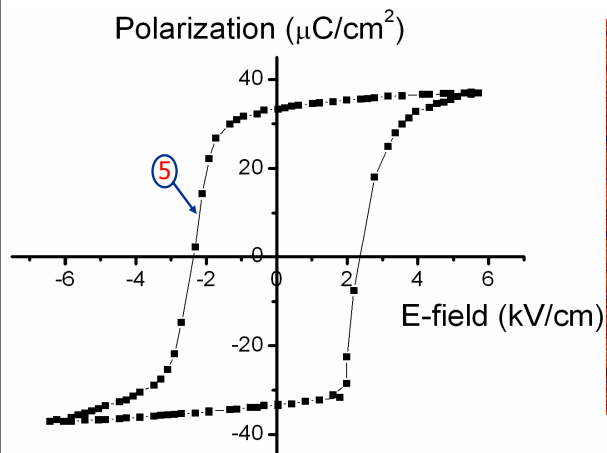
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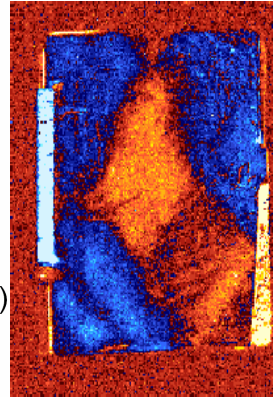
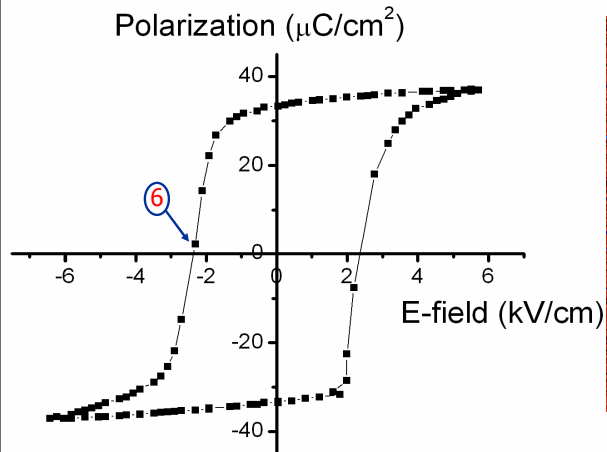
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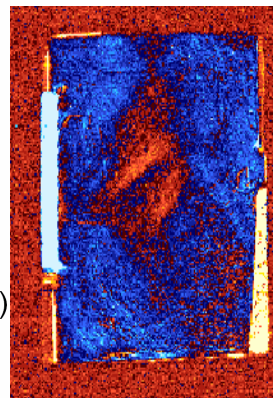
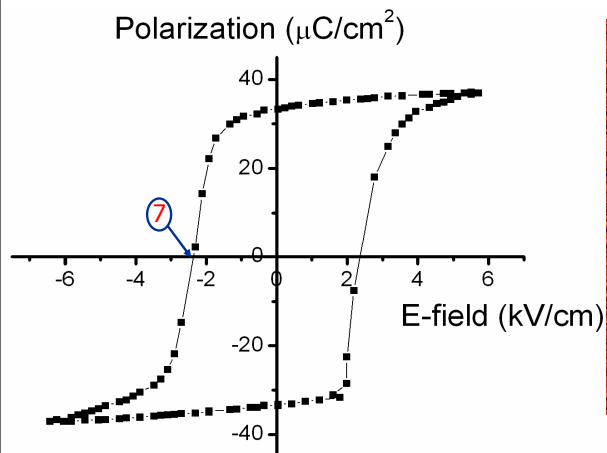
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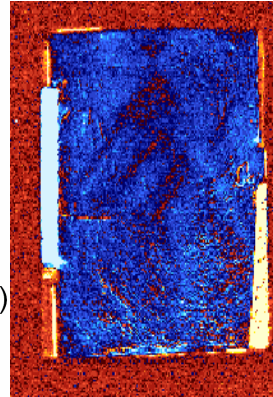
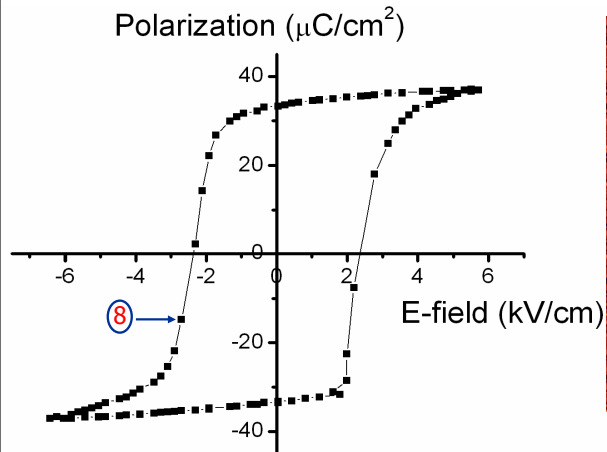
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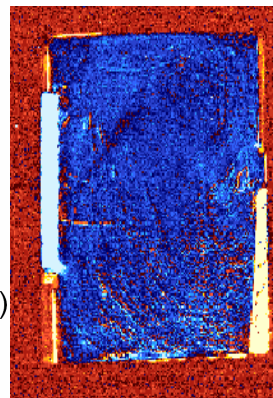
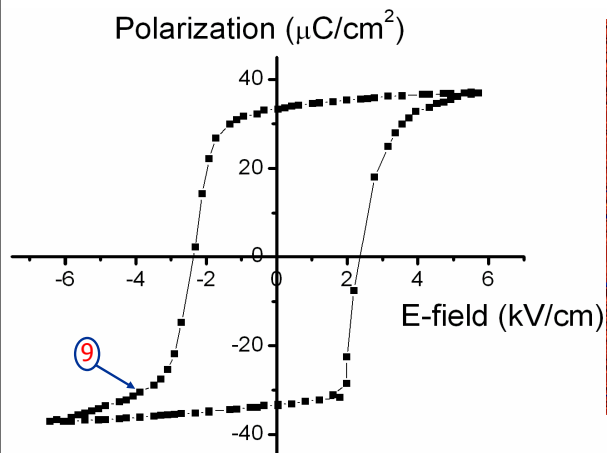
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Polarization vs. Field



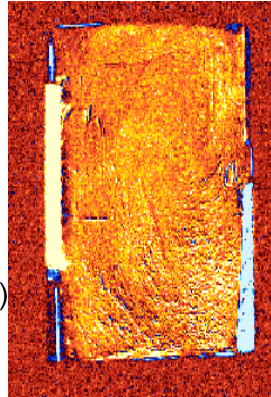
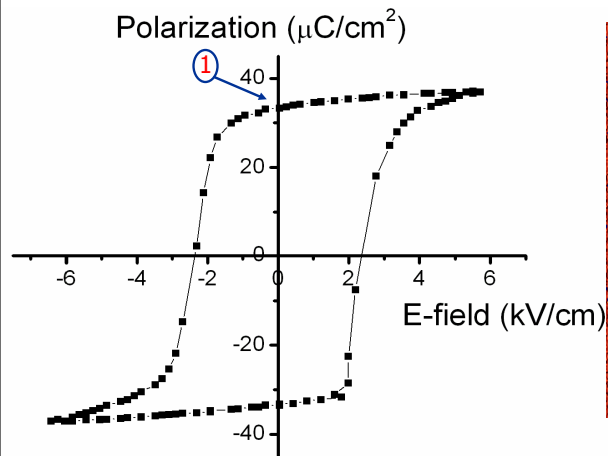
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Polarization vs. Field



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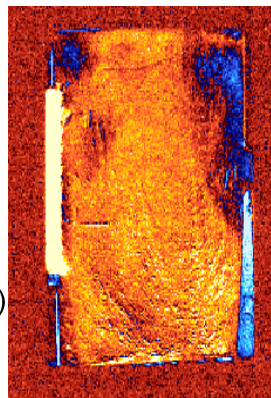
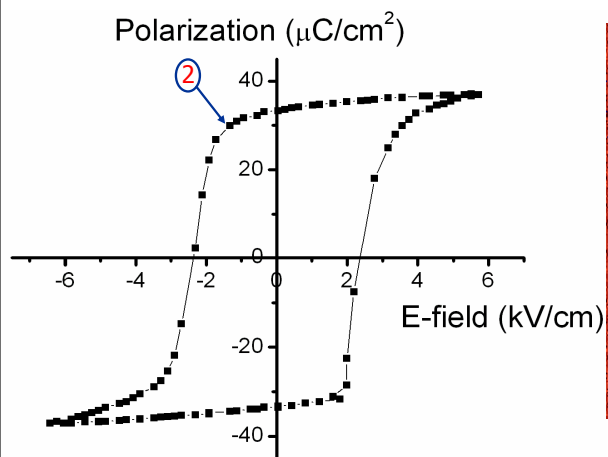
Polarization vs. Field



•Measured by RT66A

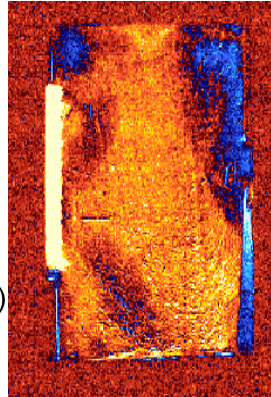
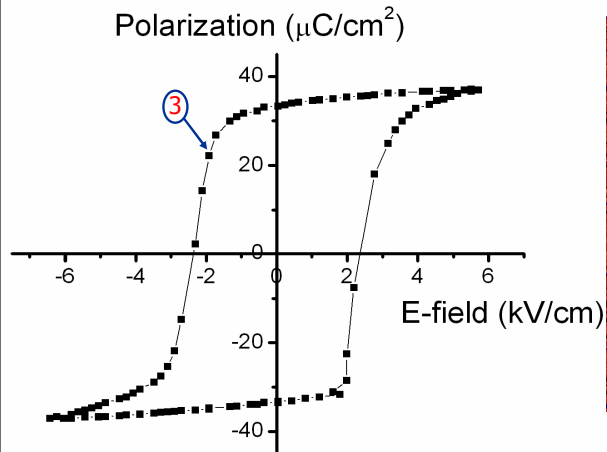
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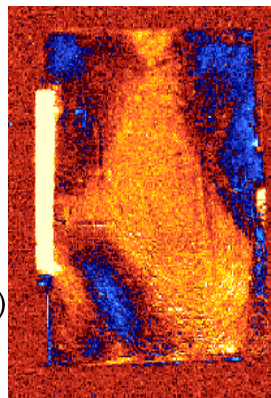
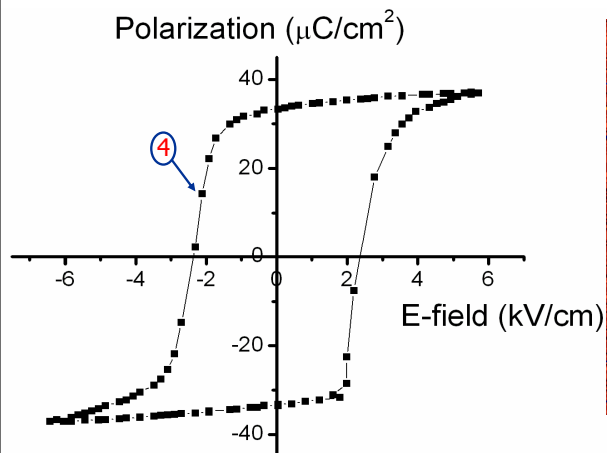
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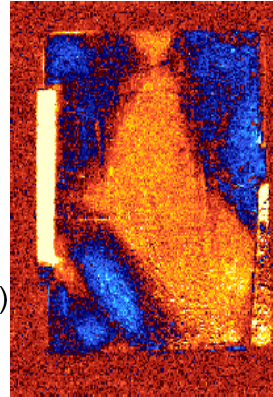
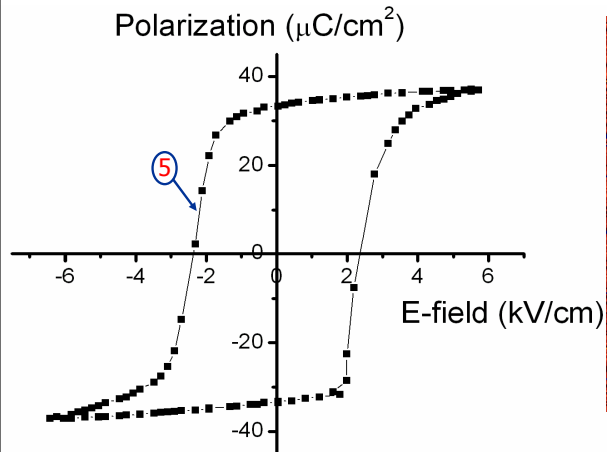
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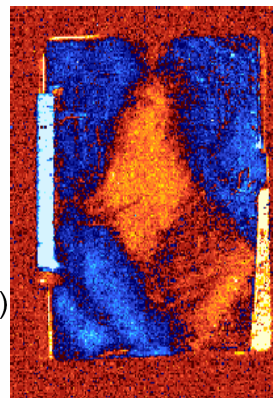
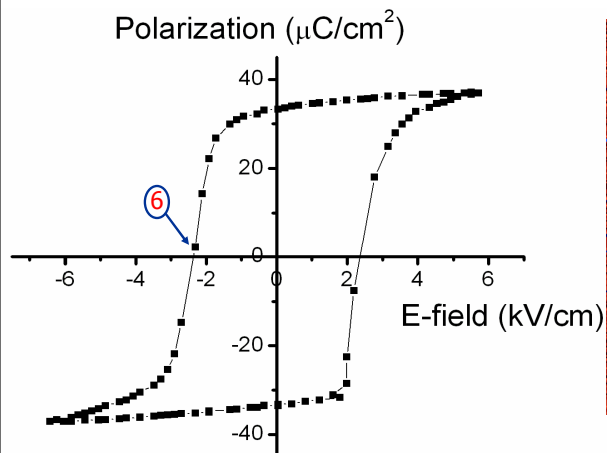
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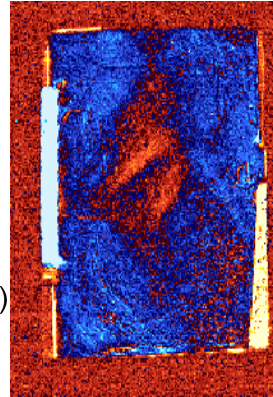
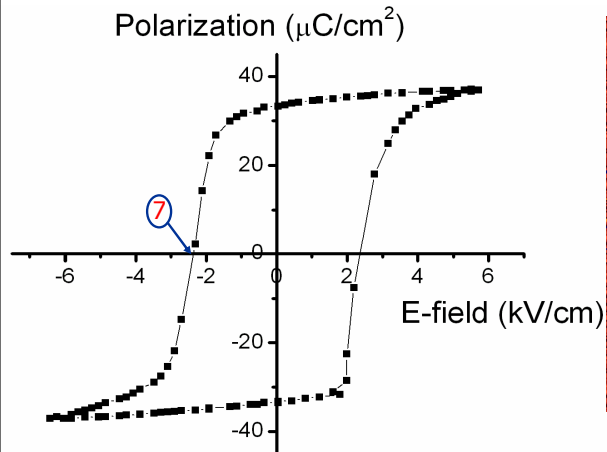
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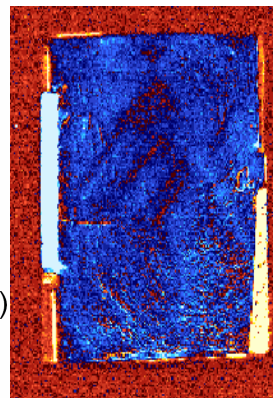
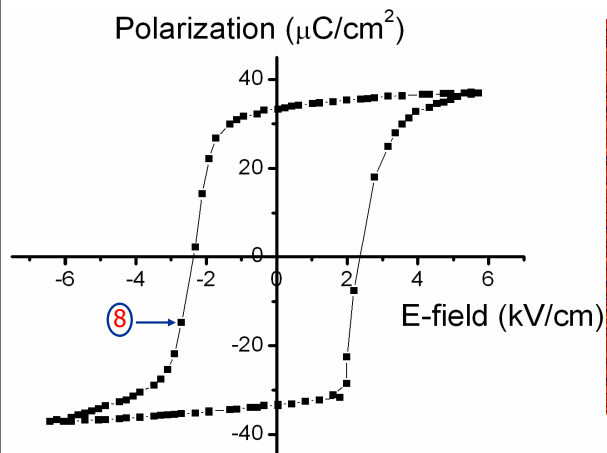
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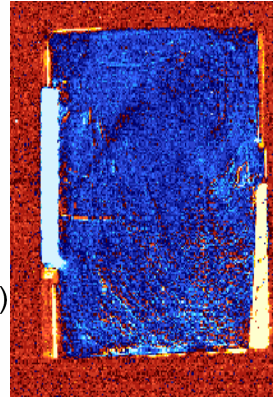
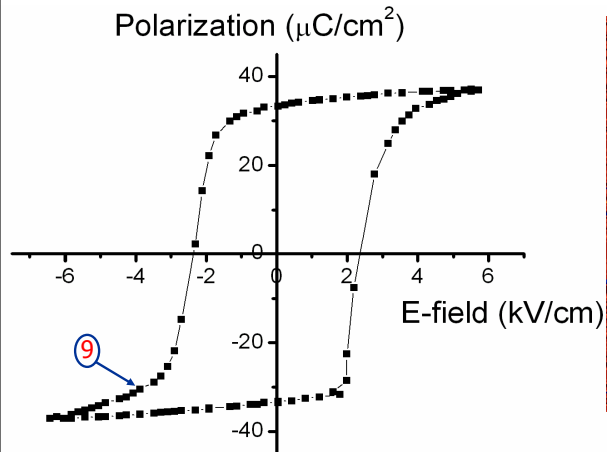
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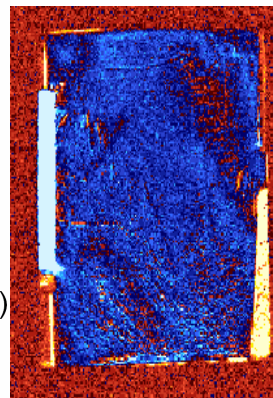
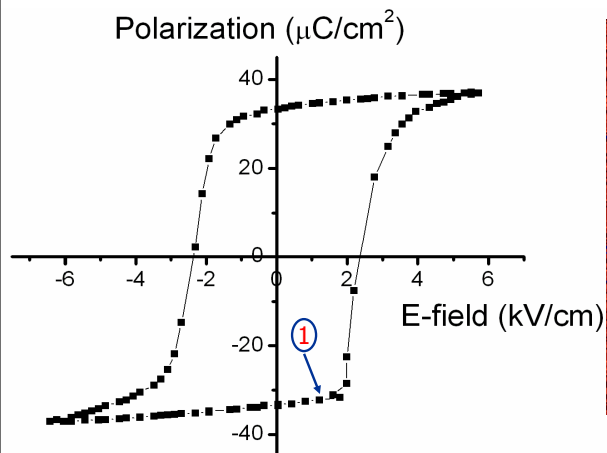
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Polarization vs. Field



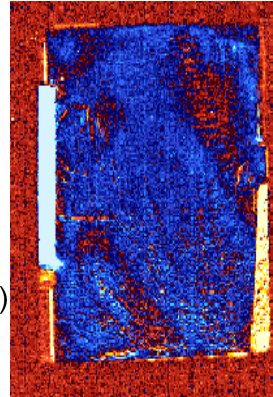
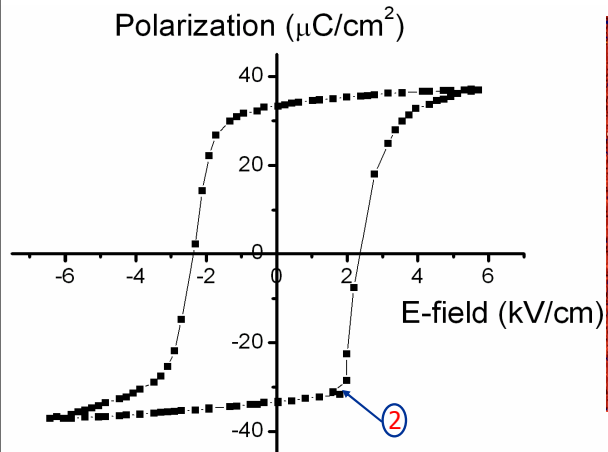
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Back switching



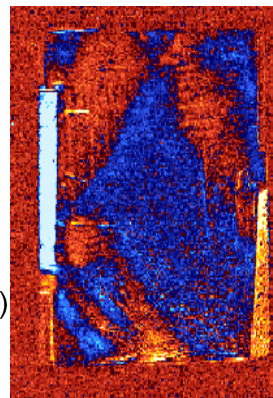
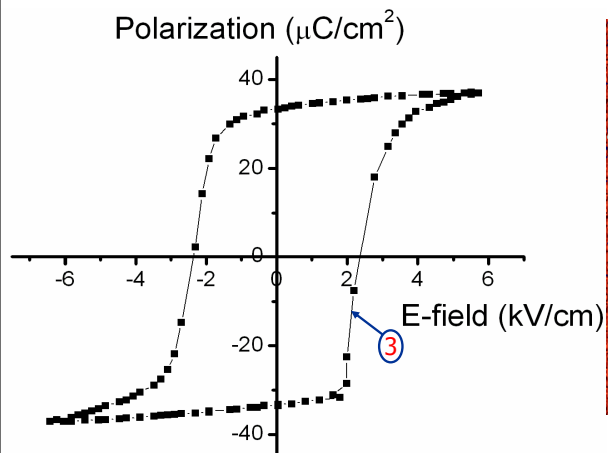
44

Back switching



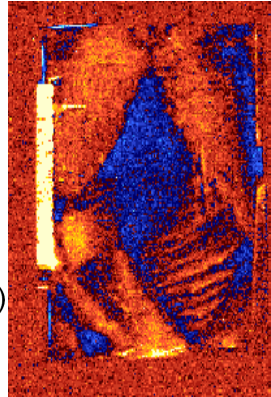
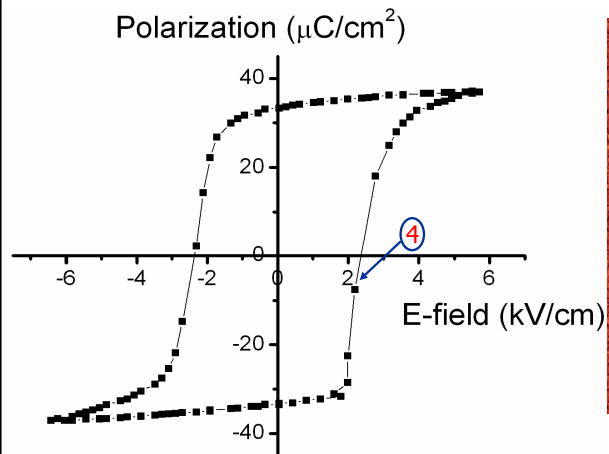
45

Back switching



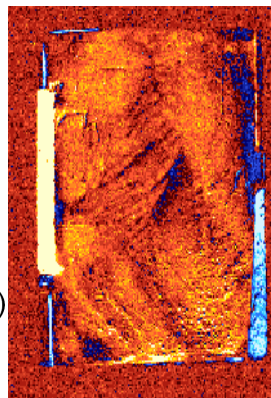
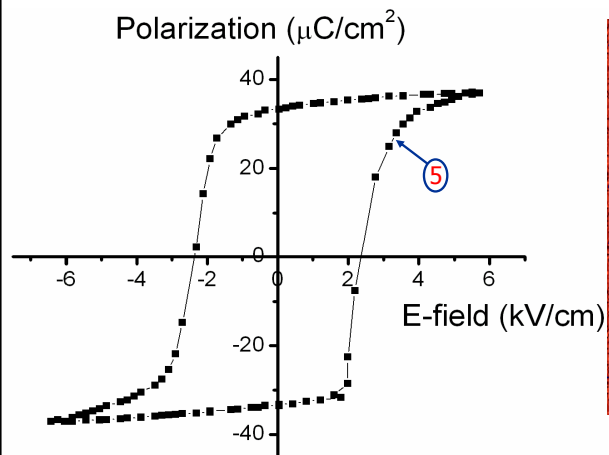
46

Back switching



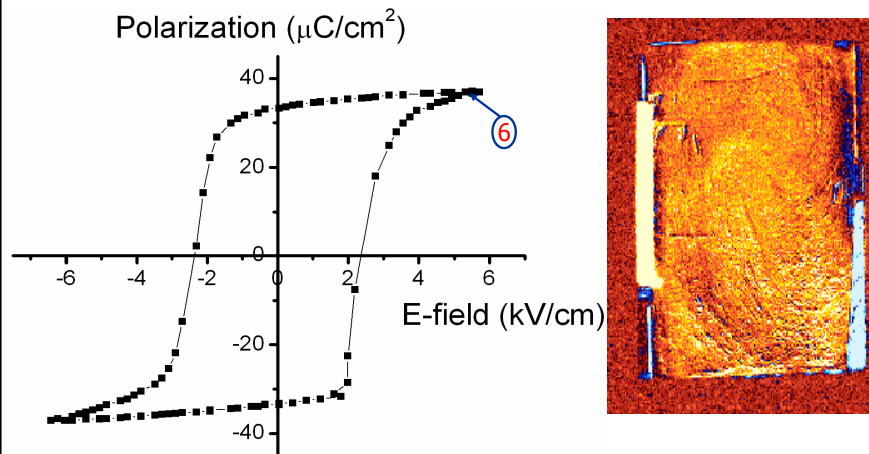
47

Back switching



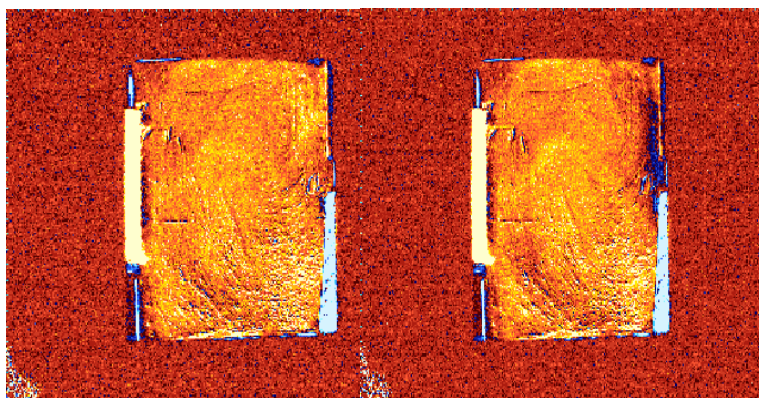
48

Back switching



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Initial and final poling states

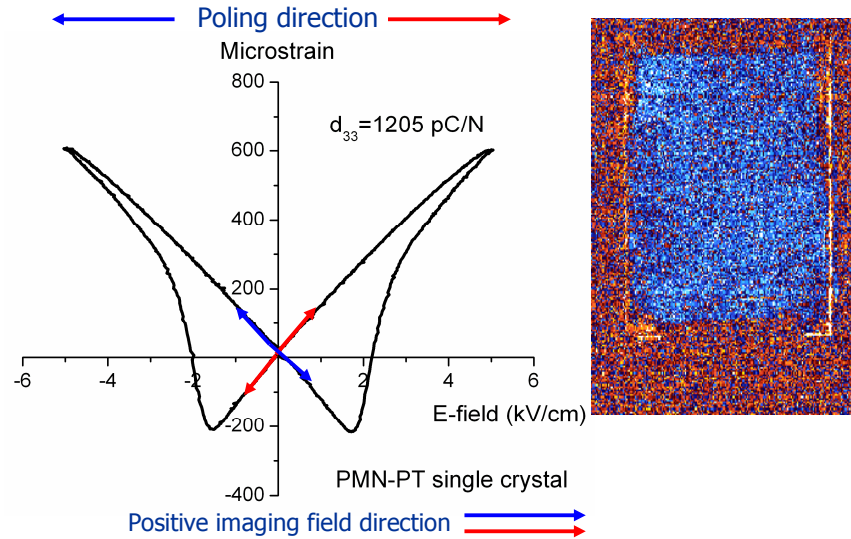


Initially poled state

Final state after switching the polarization twice

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Strain vs. Field



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Conclusions

- A new method of thermal imaging was used to observe polarization reversal.
- The method gives useful information for the extent of poling over large areas, and can be used for quality control.
- Polarization reversal started at the edges of the crystal and proceeded towards the center.
- The sign of polarization can be determined unlike optical microscopy.

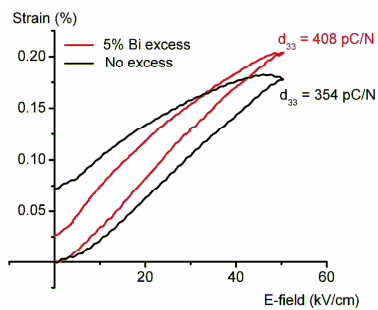
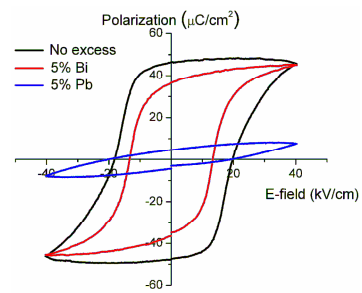
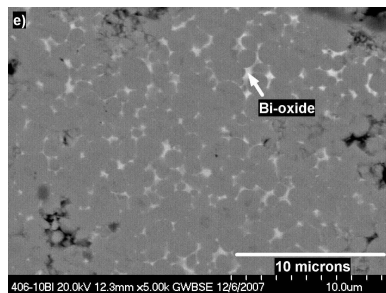
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- Prof. David Payne
- H.C Materials – Single crystals
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- Scott R. Wilson – XRD
- Prof. Jian-Min Zuo, Dr. Chang Lei and Khalid Hattar - TEM
- Dr. Tom Mackin and Chris Deiter – Electrothermal Imaging

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High Temperature Piezoelectrics

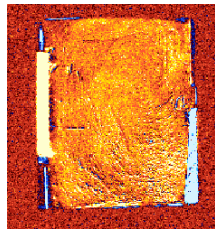


IEEE-ISAF
Wednesday, Feb 27th 11am

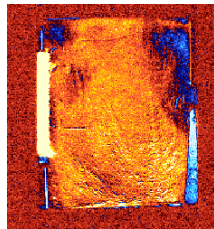
Piezoelectrics Session
(Anasazi South Room)

54

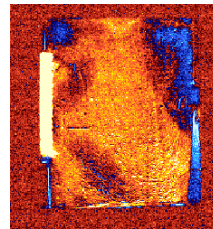
Polarization reversal



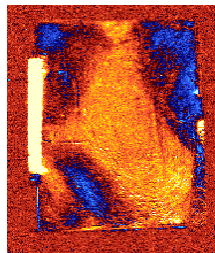
Poled sample



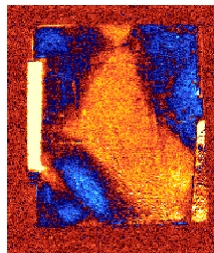
-200 V, 5 sec



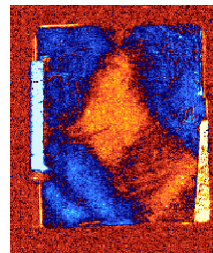
-250 V, 5 sec



-300 V, 5 sec



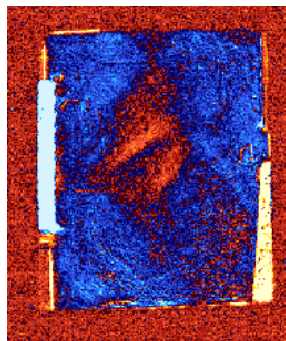
-300 V, 10 sec



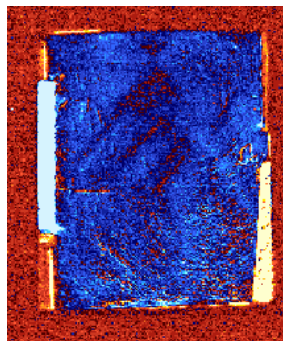
-350 V, 5 sec

55

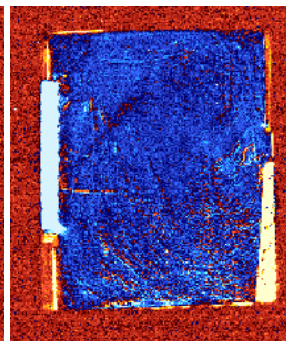
Polarization Reversal (2)



-350 V, 5 sec



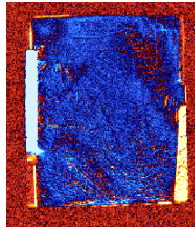
-375 V, 5 sec



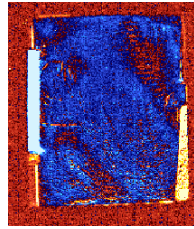
fully reversed at -375 V

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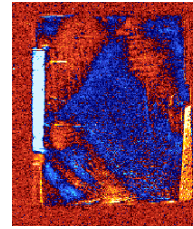
Back switching



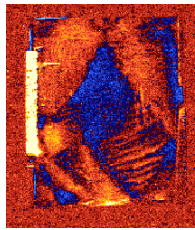
250 V, 5 sec



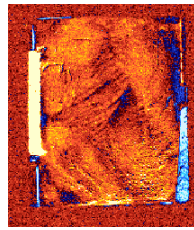
300 V, 5 sec



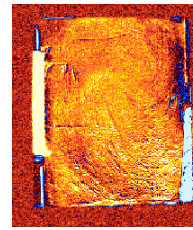
350 V, 5 sec



350 V, 5 sec



500 V, 5 sec



fully reversed at 750 V